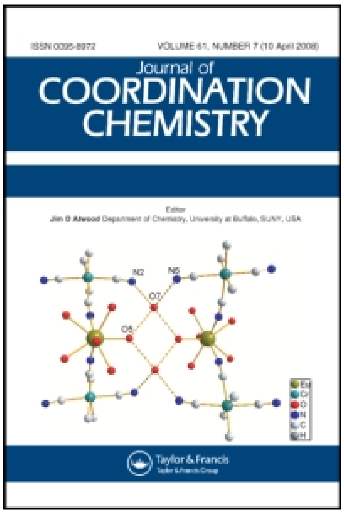

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

PROTONATION CONSTANTS OF 2,6-BIS(2-PYRIDYL)PYRIDINE AND 2,4,6-TRIS(2-PYRIDYL)-1,3,5-TRIAZINE AND FORMATION CONSTANTS OF THEIR BINARY AND TERNARY IRON(II) COMPLEXES

Alfred A. Schilt[a]; Sy-Wen Wong[a]
[a] Department of Chemistry, Northern Illinois University, DeKalb, Illinois, U.S.A

To cite this Article Schilt, Alfred A. and Wong, Sy-Wen(1984) 'PROTONATION CONSTANTS OF 2,6-BIS(2-PYRIDYL)PYRIDINE AND 2,4,6-TRIS(2-PYRIDYL)-1,3,5-TRIAZINE AND FORMATION CONSTANTS OF THEIR BINARY AND TERNARY IRON(II) COMPLEXES', Journal of Coordination Chemistry, 13: 4, 331 — 339
To link to this Article: DOI: 10.1080/00958978408073887
URL: http://dx.doi.org/10.1080/00958978408073887

J. Coord. Chem., 1984, Vol. 13, p. 331-339
0095-8972/84/1304-0331 $18.50/0

PROTONATION CONSTANTS OF 2,6-BIS(2-PYRIDYL)PYRIDINE AND 2,4,6-TRIS(2-PYRIDYL)-1,3,5-TRIAZINE AND FORMATION CONSTANTS OF THEIR BINARY AND TERNARY IRON(II) COMPLEXES

ALFRED A. SCHILT and SY-WEN WONG
Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.

(Received February 1, 1984; in final form April 10, 1984)

Equilibrium constants involving the ternary mixed ligand iron(II) complex $[Fe(TPTZ)(terpy)]^{2+}$, determined spectrophotometrically at 23° and $\mu = 0.5\ M$, are reported. Acidity constants of the protonated ligands and formation constants of the binary iron(II) complexes $[Fe(TPTZ)_2]^{2+}$ and $[Fe(terpy)_2]^{2+}$, measured as an adjunct to determining the ternary complex constants, are also reported. The results are of interest in elucidating mixed-ligand complexation effects as well as in confirming or correcting previously reported equilibrium constants of the binary complexes.

INTRODUCTION

An interesting facet in the study of mixed ligand complexes concerns the relationships between the properties of a ternary complex and those of the two binary complexes from which it is derived. One approach to such information involves measurement and comparison of formation constants. Studies of this kind have been summarized in an extensive review by Marcus and Eliezer.[1] Of particular interest is the mixing constant, which reveals any "excess stability" or "instability" associated with the mixed complex in comparison with the binary species.

Our interest in the analytical applications of 2,6-bis(2-pyridyl)pyridine (terpy) and 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) led us to study the mixed ligand iron(II) complex of these two closely related ligands, in particular its formation constant and the mixing constant K_M, the equilibrium constant of the reaction between the two binary species to give the ternary complex as in the following equation.

$$[Fe(TPTZ)_2]^{2+} + [Fe(terpy)_2]^{2+} \rightleftharpoons 2\ [Fe(TPTZ)(terpy)]^{2+}$$

This necessitated redetermination of the formation constants of the binary complexes as well as the acidity constants of the protonated ligands. Our results, reported here, indicate that formation of the mixed complex involves a small loss in stabilization energy, due perhaps to a loss in solvation energy or possibly to an interaction between the slightly dissimilar ligands.

EXPERIMENTAL

Materials and instruments

The purity of TPTZ and terpy, both obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio, was confirmed by elemental analysis and melting points. Standard iron solutions were prepared by dissolving accurately weighed samples of electrolytic iron in hydrochloric acid and diluting to the desired volume. Measurement of pH was made with a Corning 7 pH meter and a calomel-glass combination electrode. Ultraviolet spectra were recorded using a Varian 2290 spectrophotometer and visible spectra with a Cary 14 spectrophotometer. Data calculation and plotting were made with an Altos computer and a Watanabe WX4671 plotter.

Determination of acidity constants of protonated ligands

Ultraviolet spectra were recorded of solutions of different pH that contained identical concentrations of TPTZ (2.00×10^{-5} *M*) or terpy (4.0×10^{-5} *M*). These were prepared using sufficient amounts of ammonium acetate and hydrochloric acid or ammonia to adjust the pH yet maintain the ionic strength at 0.10 *M*. Acidity constants were deduced from the spectral data using non-linear least-squares analysis[2] to obtain best-fit values for the parameters K_1, K_2, ε_L, ε_{HL^+}, and $\varepsilon_{H_2L^{+2}}$ in equation (*1*), derived from Beer's law and assuming additivity of absorbances,

$$A = \frac{C_L}{K_1K_2 + [H^+]K_1 + [H^+]^2}\,(K_1K_2\varepsilon_L + K_1[H^+]\varepsilon_{HL^+} + [H^+]^2\varepsilon_{H_2L^{+2}}) \qquad (1)$$

where A is the absorbance at a given wavelength for a 1 cm path, C_L is the total ligand concentration ($C_L = [L] + [HL^+] + [H_2L^{+2}]$), K_1 is the acid dissociation constant of H_2L^{+2}, K_2 is the constant for HL^+, and the molar absorptivities of the three species are represented by ε_L, ε_{HL^+} and $\varepsilon_{H_2L^{+2}}$.

Determination of formation constants of binary complexes

Overall formation constants, β_2, were calculated using non-linear least-squares analysis [2] (absorbance as the dependent and pH as the independent variable) to obtain best-fit values for the parameters β_2 and ε_{ML_2} in solving the following cubic equation, derived from Beer's law, stoichiometry and equilibrium equations

$$\delta^3 - \left(\frac{2+2R}{R}\right)\delta^2 + \left(\frac{4+R}{R} + \frac{1}{\alpha_L^2\beta C_L^2}\right)\delta - \frac{2}{R} = 0 \qquad (2)$$

$$\text{where } \alpha_L = \frac{[L]}{C_L} = \frac{K_1K_2}{K_1K_2 + [H^+]K_1 + [H^+]^2} \qquad (3)$$

$$\text{and } \delta = \frac{2[ML_2]}{C_L} = \frac{2A/\varepsilon_{ML_2}}{C_L}\ ;\ R = C_L/C_M\ ;\ C_L \text{ and } C_M$$

are analytical concentrations of L and M, respectively; K_1 and K_2 are the acid dissociation constants of the diprotonated ligand.

Four different series of aqueous solutions were prepared and absorption spectra recorded from 350 to 700 nm to obtain the spectrophotometric data necessary for the above calculations. One series of solutions, 4.15×10^{-5} *M* in iron(II) and containing various concentrations of TPTZ, was prepared by adding 5.00 cm^3 of 4.15×10^{-4} *M* iron(II) chloride into 50 cm^3 volumetric flasks, 2 cm^3 of 10% hydroxylamine hydrochloride, 10 cm^3 of pH 4.5 buffer solution (acetic acid-ammonium acetate), and different amounts of 3.98×10^{-4} *M* TPTZ to each flask, followed by sufficient distilled water to dilute to volume. A second series of solution, 8.30×10^{-5} *M* in iron(II) and containing various amounts of terpy, was prepared in the same way. A third series was prepared to be 4.15×10^{-5} *M* in Fe(TPTZ)$^{2+2}$ and with various amounts of hydrochloric acid added to each to adjust to different desired pH values. The fourth series was prepared to be 4.15×10^{-5} *M* in Fe(terpy)$_2^{+2}$ and with various amounts of hydrochloric acid to achieve the desired pH values.

Determination of complexation constants of the ternary complex

Equilibria and constants of interest for the ternary complex (using symbols M, A, and B to represent Fe^{+2}, TPTZ and terpy, respectively) are the following equations (*4*)-(*7*).

$$M + A + B \rightleftharpoons MAB; \ K_f(MAB) \qquad (4)$$

$$MA_2 + B \rightleftharpoons MAB + A; \ K_{(+B\text{-}A)} \qquad (5)$$

$$MB_2 + A \rightleftharpoons MAB + B; \ K_{(+A\text{-}B)} \qquad (6)$$

$$1/2 \ MA_2 + 1/2 \ MB_2 \rightleftharpoons MAB; \ K_M \qquad (7)$$

The ternary equilibrium constants are related to the binary formation constants $\beta_{2(MA_2)}$ and $\beta_{2(MB_2)}$ as shown in (*8*)-(*11*)

$$K_M = K_{f(MAB)}/(\beta_{2(MA_2)}\beta_{2(MB_2)})^{1/2} \qquad (8)$$

$$K_M = (K_{(+B\text{-}A)}K_{(+A\text{-}B)})^{1/2} \qquad (9)$$

$$K_{f(MAB)} = \beta_{2(MA_2)}K_{(+B\text{-}A)} \qquad (10)$$

$$K_{f(MAB)} = \beta_{2(MB_2)}K_{(+A\text{-}B)} \qquad (11)$$

Thus, if both binary formation constants and any one of the ternary equilibrium cosntants are known, all other ternary equilibrium constants can be calculated. Four different approaches are possible. Specifically, measurements can be made of any one of the equilibria (*4*), (*5*), (*6*) or (*7*), whichever best lends itself to precise determination of its equilibrium constant. All four approaches were attempted in this research, but only one proved sucessful. This involved spectrophotometric determination of K_M by the method of continuous variations. For this purpose a series of solutions was prepared in which the ratio of concentration of the two binary complexes FeA$_2^{+2}$ and FeB$_2^{+2}$ was varied while holding their sum constant at 3.91×10^{-5} *M*. Each solution was 0.1 *M* in ammonium acetate to maintain the pH at 7.0. It was also found necessary to adjust the solutions to be 3.91×10^{-5} *M* in excess TPTZ to prevent dissociation of Fe(TPTZ)$_2^{+2}$. The spectra of each solution was recorded, and the data were employed to calculate K_M, using the following equation, derived from Beer's law and stoichiometric relationships,

$$K_M = (\Delta A/k)/[C_{MA_2} - \Delta A/2k)^{1/2}(C_{MB_2} - \Delta A/2k)^{1/2}] \qquad (12)$$

where $\Delta A = A_M - A_C = A_M - (\varepsilon_{MA_2} C_{MA_2} + \varepsilon_{MB_2} C_{MB_2})$; A_M = measured absorbance of solution at wavelength selected; A_C = absorbance predicted if no mixed ligand complex forms; $k = \varepsilon_{MAB} - 1/2 \ (\varepsilon_{MB_2} + \varepsilon_{MA_2})$; ε_{MA_2}, ε_{MB_2} and ε_{MAB_2} are molar absorptivities of the binary and ternary complexes at wavelength selected, and C_{MA_2} and C_{MB_2} are the initial molar concentrations of the binary complexes on mixing prior to formation of any ternary complex.

Molar absorptivity values for the binary complexes were determined from spectra of accurately prepared solutions. Values for the ternary complex MAB were deduced from absorbance measurements of solutions with the same initial concentration of $Fe(TPTZ)_2^{+2}$ to which various known amounts of terpy had been added. A plot of the data, as for example in Figure 3, yielded by extrapolation of the linear regions an intersection at a mole ratio of unity. The absorbance at this point corresponds to that due entirely to the ternary complex. A value of 10,600 M^{-1} cm^{-1} at 596 nm was thus found for MAB. At this same wavelength, molar absorptivities of 22,600 and 2,410 were found for MA_2 and MB_2, respectively.

RESULTS AND DISCUSSION

The ultraviolet spectra of TPTZ as a function of pH indicate that at least two different protonated species are formed over the pH range 0.3 - 7.0. A band at 290 nm for acidic solutions shifts with increasing pH to 283 nm, the change in pH required for completion of the spectral changes is grater than that expected for a monoprotonated species, and there is not a distinct well-defined isosbestic point (only the semblance of one). If we therefore assume that only two protonated and one unprotonated species exist in the solutions, then the molar absorptivities of the diprotonated and unprotonated species can be readily deduced, one from the data at high pH and the other at very low pH. thus, a plot of absorbance at 250 nm versus pH (Figure 1) reveals molar absorptivity values of 24,400 for TPTZ and

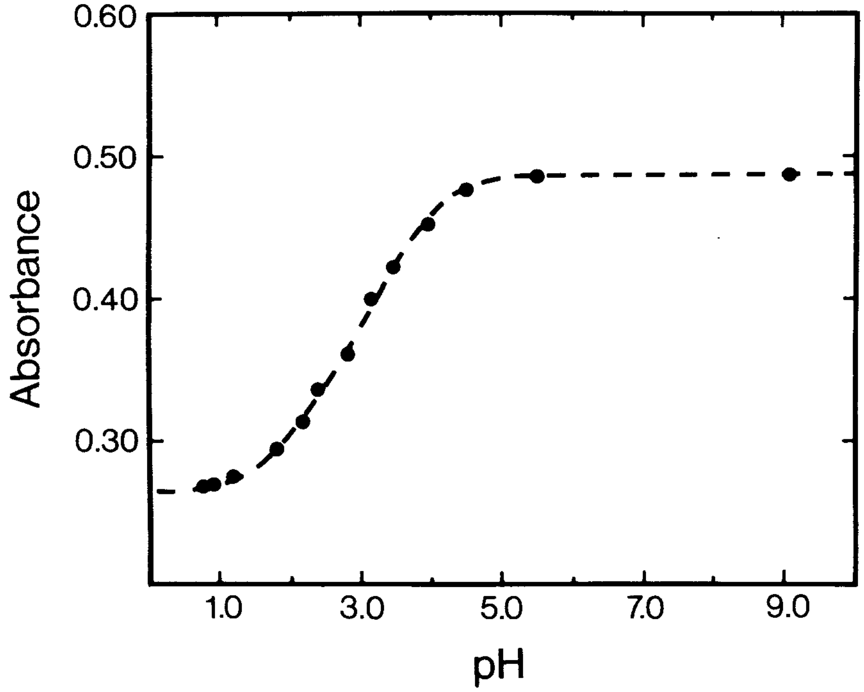

FIGURE 1 Absorbance of TPTZ (2.00×10^{-5} M; $\mu = 0.1$ M) at 250 nm versus pH. Solid circles indicate experimental data, and the dashed line depicts the theoretical curve obtained based on the two "best-fit" pK^a values.

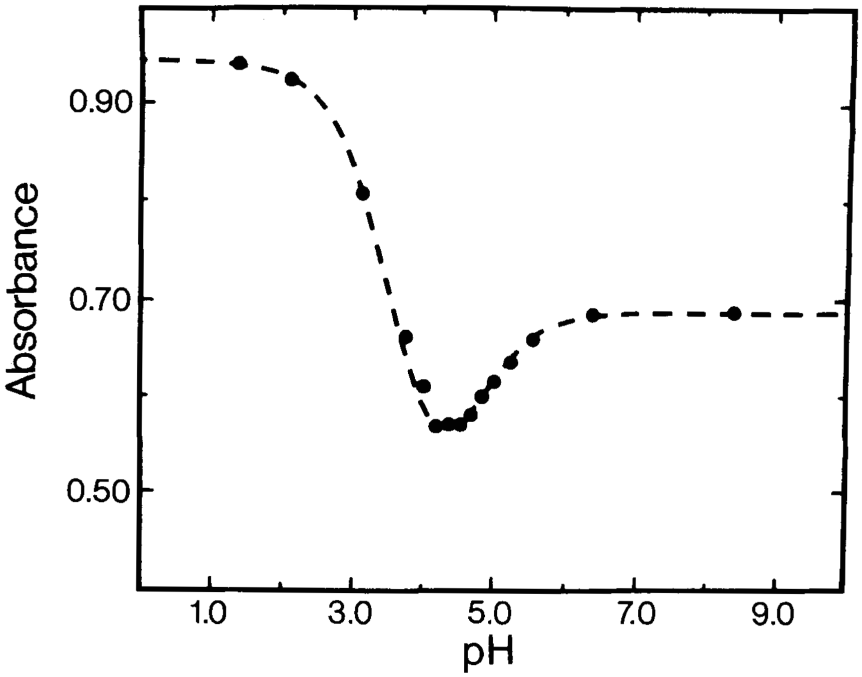

FIGURE 2 Absorbance of terpy (4.00×10^{-5} M; $\mu = 0.1$ M) at 287 nm versus pH. Solid circles indicate experimental data, and the dashed line depicts the theoretical curve obtained based on the two "best-fit" pK^{a} values.

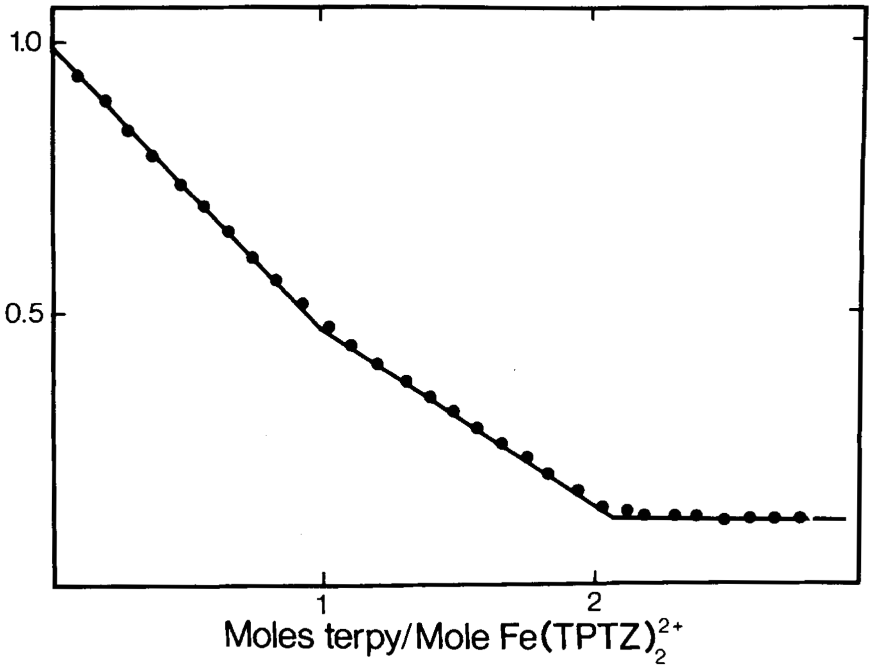

FIGURE 3 Absorbance at 596 nm versus moles of terpy added per mole of [Fe(TPTZ)$_2$]$^{2+}$ initially present (4.32×10^{-5} M; to determine the absorbance and molar absorptivity of the ternary complex (formed at a mole ratio of 1.00).

13,200 for H_2TPTZ^{+2}. Least-squares analysis of the pH-absorbance data as described in the Experimental section, yielded values of ε_L = 24,310 ± 140, ε_{HL} = 18,000 ± 1,000, ε_{H_2L} = 13,370 ± 120, pK_1 = 2.19 ± 0.16, and pK_2 = 3.40 ± 0.13. The best-fit values of ε_L and ε_{H_2L} agree closely with the experimental limiting values indicated by Figure 1. The assumption as well as the validity of these results is confirmed by the close match obtained between experimental and calculated absorbance data at different pH values, as evidenced by Figure 1.

Ultraviolet spectra obtained for the terpy solutions provide good evidence for the existence of two protonated species. Solutions of pH 1-4 yielded spectra with three bands and four distinct isosbestic points (at 346.5, 308, 293.5 and 275.5 nm). Solutions of pH 4.2 - 9.7 yielded two-band spectra and two distinct isosbestic points at 309.5 and 240.5 nm. Following the same approach as for TPTZ, the best-fit values obtained for the terpy constants are ε_L = 17,170 ± 90, ε_{HL} = 11,450 ± 310, ε_{H_2L} = 23,450 ± 90 (all at 287 nm), pK_1 = 3.57 ± 0.04, and pK_2 = 4.71 ± 0.06. Close agreement between observed and calculated absorbance data is evidenced by the plot shown in Figure 2. Particularly noteworthy is the close agreement of the pK values obtained here spectrophotometrically with those determined potentiometrically by Kim and Nancollas (see Table IV).[11]

Data and results obtained for the determination of the overall formation constants of the binary complexes $Fe(TPTZ)_2^{+2}$ and $Fe(terpy)_2^{+2}$ are compiled in Tables I and II, respectively. The lower stability of the TPTZ iron(II) chelate (log

TABLE I
Formation constant of $Fe(TPTZ)_2^{+2}$ at $\mu = 0.5\,M$ and T = 23°
($C_{Fe} = 4.15 \times 10^{-5}\,M$ and $C_{TPTZ} = 8.76 \times 10^{-5}\,M$).

pH	Absorbance at 593 nm		Error
	Experimental	Calculated†	
2.00	0.139	0.124	−0.015
2.24	.310	.310	.000
2.72	.615	.632	.017
3.45	.814	.814	.000
3.76	.844	.839	− .005
3.85	.847	.844	− .003
4.05	.854	.851	− .003

†From Equation (*2*) for which the following best-fit parameters were deduced: ε_{ML_S} = 22,500 ± 200, log β_2 = 11.05 ± 0.03.

TABLE II
Formation constant of $Fe(terpy)_2^{+2}$ at $\mu = 0.5\,M$ and T = 23°
($C_{Fe} = 4.15 \times 10^{-5}\,M$ and $C_{terpy} = 8.76 \times 10^{-5}\,M$).

pH	Absorbance at 552 nm		Error
	Experimental	Calculated†	
0.40	0.004	0.007	0.003
0.45	.009	.011	.002
0.53	.020	.022	.002
0.68	.051	.065	.014
0.79	.109	.120	.011
0.92	.206	.200	− .006
1.15	.351	.329	− .028
1.86	.470	.482	.012

†From Equation (*2*) for which the following best-fit parameters were deduced: ε_{ML_2} = 11,900 ± 300, log β_2 = 21.26 ± 0.06.

TABLE III
Step-wise and conditional formation constants of Fe(TPTZ)$_2$$^{+2}$ at pH = 4.50, μ = 0.5 *M*, T = 23° (C_{FE} = 4.15 × 10^{-5} *M*).

C_{TPTZ} × 10^5	R	Absorbance at 593 nm	Degree of formation, α_2	Log K'_f
1.59	0.384	0.141	0.150	10.18
3.18	.768	.303	.324	10.28
4.78	1.15	.469	.500	10.41
6.37	1.53	.635	.677	10.57
7.16	1.72	.714	.761	10.65
7.56	1.82	.752	.802	10.69
7.96	1.92	.787	.840	10.73
8.36	2.02	.824	.879	10.81
8.76	2.11	.855	.912	10.86
9.15	2.21	.883	.942	10.96
9.55	2.30	.898	.958	10.95
11.14	2.69	.925	.987	10.92
12.74	3.07	.933	.995	10.98

Results of least-squares analysis (best-fit parameters for Equation (*15*)): ϵ_{ML_2} = 22,900 ± 100, log k_1 = 4.81 ± 0.07, log k_2 = 6.26 ± 0.04, log k_1k_2 = 11.07 = log β_2 (*cf* Table I value of 11.05).

TABLE IV
Comparison of results with literature values.

Ligand	Acidity constants		Iron(II) complex	Conditions		
	− Log K_1 ($H_2L^{+2} \rightleftharpoons H^+ + HL^+$)	− Log K_2 ($HL^+ \rightleftharpoons H^+ + L$)	Log β_2 ($Fe^{+2} + 2L \rightleftharpoons FeL_2^{+2}$)	μ/*M*	T/°	Ref.
TPTZ	2.19	3.40	11.05	0.1	23	This work
		3.10	10.24	0.1	25	3
	2.7	3.5	12.4	0.1	25	4
	2.82	2.8		0.2	25	5
			11.5		20	6
Terpy	3.57	4.71	21.26	0.1	23	This work
	(7.1-pK_2)	(7.1-pK_1)	18.0			7
	2.64	4.33	20.4	0.1	23	8
	2.59	4.16			--	9
	3.99	4.69		0.1	25	10
	3.53†	4.75†		0.1	25	11

†Values of the mixed constants calculated from the concentration constants and activity coefficients reported.

β_2 = 11.05 ± 0.03) enabled more precise spectrophotometric determination of its formation constant than did the much more stable terpy iron(II) chelate (log β_2 = 21.26 ± 0.06).

Data in Table III reveal that values of log K'_f at pH 4.5 increase with increasing values of R, the ligand to metal ratio. This trend indicates that formation of the monochelate Fe(TPTZ)$^{+2}$ is appreciable and should not be ignored at R values less than 3. The data proved amenable for calculating the stepwise formation constants k_1 and k_2 for Fe(TPTZ)$^{+2}$ and Fe(TPTZ)$_2$$^{+2}$, respectively. The following equations were derived for this purpose from Beer's law, stoichiometry and equilibrium constant expressions (assuming that only Fe(TPTZ)$_2$$^{+2}$ absorbs at 593 nm),

$$\alpha_2 + k_1\alpha_2[L] + k_1k_2(\alpha_2-1)[L]^2 = 0 \qquad (13)$$

$$[L] = \frac{C_L\alpha_L}{R}(R-1-\alpha_2) \qquad (14)$$

where

$$\alpha_2 = \frac{[ML_2]}{C_M} = \frac{A_{593}/\epsilon_{ML_2}}{C_M}, R = C_L/C_M, \alpha_L = [L]/C_L, [L] = [TPTZ], [ML_2] =$$

$[Fe(TPTZ)_2{}^{+2}]$, and C_L and C_M are total concentrations of TPTZ and iron(II), respectively. Experimental values obtained for A_{593} at known C_M, C_L, and $[H^+]$ (hence α_L known also) thus enabled calculation of k_1, k_2, and ϵ_{ML_2}. For the non-linear least-squares analysis the following cubic equation was employed, derived by combining equations (*13*) and (*14*).

$$\alpha_2^3 + \left(3-2R - \frac{1}{C_M k_2 \alpha_L}\right)\alpha_2^2 + \left(3 + R^2 - 4R - \frac{1-R}{C_M k_2 \alpha_L} + \frac{1}{C_M^2 k_1 k_2 \alpha_L^2}\right)\alpha_2$$

$$+ (R-1)^2 = 0 \qquad (15)$$

Pertinent data and results are compiled in Table III. It is reassuring to note the good agreement between the results obtained for β_2 and ϵ_{ML_2} in this experiment and those listed in Table I. A further note of interest is the finding that k_2 is consdierably larger than k_1, an observation that is consistent with the change from high spin to low spin on going from the mono-to the bis-chelate, analogous to the results found for the iron(II) chelate of 1,10-phenanthroline.[12]

Direct measurement of the overall formation constant K_f of the ternary complex proved impractical because mixtures of Fe^{+2}, terpy and TPTZ invariably yielded binary as well as the ternary complex, greatly complicating accurate spectrophotometric analysis of the mixtures. Attempts to measure the substitution constants $K_{+A\text{-}B}$ and $K_{+B\text{-}A}$ revealed that substitution of TPTZ for bound terpy was too slight ($K_{+A\text{-}B} < 10^{-3}$) and substitution of terpy for TPTZ was too pronounced ($K_{+B\text{-}A} \} 10^{-3}$) for accurate spectrophotometric determination of the constants. Dimensionless constants such as these are difficult to determine spectrophotometrically if their magnitude lies outside the range $10^{-3} - 10^{+3}$, because no means of manipulating the equilibrium exists, such as adjustment of PH to enable spectrophotometric determination of dissociation constants of weak acids or bases. Fortunately, measurement of the mixing constant K_M proved practical by the method of continuous variations. Experimental data and results obtained by this approach are compiled in Table IV. The average of the values

TABLE V

Mixing constant for the formation of $Fe(TPTZ)(terpy)^{+2}$ at $\mu = 0.1$ *M* and T = 23°.

Initial concentration × 10^5 *M*		Absorbance at 596 nm		ΔA	$[Fe(TPTZ)(terpy)^{+2}]$ × 10^6	K_M
$[Fe(TPTZ)_2{}^{+2}]$	$[Fe(terpy)_2{}^{+2}]$	Calculated	Measured			
3.24	0.669	0.7492	0.7437	−0.0055	2.8	0.22
2.57	1.34	0.6148	0.6073	−0.0075	3.8	0.23
1.90	2.01	0.4805	0.4702	−0.0103	5.3	0.31
1.82	2.09	0.4636	0.4492	−0.0144	7.4	0.47
1.74	2.17	0.4473	0.4358	−0.0115	5.9	0.36
1.07	2.84	0.3125	0.3006	−0.0119	6.1	0.44
0.40	3.51	0.1782	0.1714	−0.0068	3.5	0.40

Average $K_M = 0.39 \pm 0.06$

found for K_M is 0.394. This value together with the constants obtained for the binary complexes yielded the values for the other ternary constants, calculated from Equations (*8*), (*10*), and (*11*) of $K_{f(MAB)} = 5.57 \times 10^{15}$, $K_{+B\text{-}A} = 4.97 \times 10^{4}$, and $K_{+A\text{-}B} = 3.1 \times 10^{-6}$.

The concern as to whether or not measurement of K_M could have been adversely affected by the presence of a slight excess of TPTZ, added to discourage dissociation of $Fe(TPTZ)_2^{+2}$, can now be addressed. The very low value found for $K_{+A\text{-}B}$ indicates that the excess TPTZ (4×10^{-5} *M*) could not have reacted with $Fe(terpy)_2^{+2}$ to any measurable extent to form the ternary complex, and thus it could not have interfered in the determination of K_M.

The question as to whether or not formation of the ternary complex involves any special (non-entropy) energy terms due to mixing of the ligands can best be considered in terms of the so-called stabilization constant K_s. Since the two ligands in this case have the same denticity, K_s can be calculated as $\log K_S = \log K_M - \log 2 = -0.71$. A value less than one for K_s indicates that there is some loss in stabilization energy on mixing of the ligands to form the ternary complex. This could be due to either ligand-ligand interactions (presumably either a repulsive or geometric effect) or solvation effects (either loss in solvation energy or an unfavorable entropy change). Additional studies, at different temperatures to evaluate $\Delta H°$ and $\Delta S°$ of the reactions, might provide further insights.

ACKNOWLEDGEMENTS

The valuable assistance of R. Bruce Martin in providing the least-squares analysis and helpful suggestions is gratefully acknowledged.

REFERENCES

1. Y. Marcus and I. Eliezer, *Coord. Chem. Rev.*, **4,** 273 (1969).
2. P.R. Bevington, *"Data Reduction and Error Analysis for the Physical Sciences",* McGraw-Hill Book Co., New York, N.Y., 1969.
3. E.B. Buchanan Jr., D. Crichton and J.R. Bacon, *Talanta,* **13,** 903 (1966).
4. G.K. Pagenkopf and D.W. Margerum, *Inorg. Chem.*, **7,** 2514 (1968).
5. J. Prasad and N.C. Peterson, *Inorg. Chem.*, **10,** 88 (1971).
6. F.H. Fraser, P. Epstein and D.J. Macero, *Inorg. Chem.*, **11,** 2031 (1972).
7. W.W. Brandt and J.P. Wright, *J. Am. Chem. Soc.*, **76,** 3082 (1954).
8. R.B. Martin and J.A. Lissfelt, *J. Am. Chem. Soc.*, **78,** 938 (1956).
9. K. Nakamoto, *J. Phys. Chem.*, **64,** 1420 (1960).
10. B.R. James and R.J.P. Williams, *J. Chem. Soc.*, 2007 (1961).
11. K.Y. Kim and G.H. Nancollas, *J. Phys. Chem.*, **81,** 948 (1977).
12. H.M. Irving and D.H. Mellor, *J. Chem. Soc.*, 5222 (1962).